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NIF Anti-Reflective Coating Solutions: Preparation, Procedures and Specifications

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1.0 INTRODUCTION

The following document contains a detailed description of the preparation procedures for the antireflective coating solutions used for NIF optics. This memo includes preparation procedures for the coating solutions (sections 2.0-4.0), specifications and vendor information of the raw materials used and on all equipment used (section 5.0), and QA specifications (section 6.0) and procedures (section 7.0) to determine quality and repeatability of all the coating solutions.

There are different five coating solutions that will be used to coat NIF optics. These solutions are listed below:

1) Colloidal silica (3%) in ethanol
2) Colloidal silica (2%) in sec-butanol
3) Colloidal silica (9%) in sec-butanol (deammoniated)
4) HMDS treated silica (10%) in decane
5) GR650 (3.3%) in ethanol/sec-butanol

The names listed above are to be considered the official name for the solution. They will be referred to by these names in the remainder of this document. Table 1 gives a summary of all the optics to be coated including: 1) the surface to be coated; 2) the type of solution to be used; 3) the coating method (meniscus, dip, or spin coating) to be used; 4) the type of coating (broadband, 1ω, 2ω, 3ω) to be made; 5) # of optics to be coated; and 6) the type of post processing required (if any). Table 2 gives a summary of the batch compositions and measured properties of all five of these solutions.

Table 1: List of the optics to be coated and the coating solutions to be used.

Optic	Material	Surface I=input O=output	Solution	Coating Type	Coating Method	# of Optics Coated	Post Processing
Amplifier Windows	Borosilicate glass	I	(2)	broadband	Meniscus	~1800	Ammonia Hardening
		O	(2)	broadband			
Spacial Filter Windows (CSF/TSF)	SiO_2	I	(1)	1ω	Dip Coating	784	Ammonia Hardening
		O	(1)	1ω			
Pockels Cell Window	SiO_2	I	(1)	1ω	Dip Coating	392	Ammonia Hardening
		O	(1)	1ω			
Pockels Cell	KDP	I	(3)	1ω	Spin Coating	192	none
		O	(3)	1ω			
Beam Sample Grating	SiO_2	I	(1)	1ω*	Dip Coating	192	Ammonia Hardening
		O	(1)	1ω*			
Vacuum Window	SiO_2	I	(1)	1ω	Spin Coating	192	Ammonia Hardening
		O	(1)	1ω			
SHG	KDP	I	(5) - (4)	1ω	Spin Coating	192	(5) is cured
		O	(5) - (4)	1ω–2ω			
THG	KD*P	I	(5) – (4)	1ω–2ω	Spin Coating	192	none
		O	(4)	3ω			
Final Focus Lens	SiO_2	I	(1)	3ω	Dip Coating	192	Ammonia Hardening
		O	(1)	3ω			
Kinoform Phase Plate	SiO_2	I	(1)	1ω	Dip Coating	192	Ammonia Hardening
		O	(1)	1ω			
Debris Shield	SiO_2	I	(1)	3ω	Dip Coating	192 x # of shots	Ammonia Hardening
		O	(1)	3ω			

Solutions:

1) Colloidal silica (3%) in ethanol
2) Colloidal silica (2%) in sec-butanol
3) Colloidal silica (9%) in sec-butanol (deammoniated)
4) HMDS treated silica (10%) in decane
5) GR650 (3.3%) in ethanol/ sec-butanol

Table 2. Summary of batch compositions and properties of all coating solutions

PROPERTY	UNITS	FUSED SILICA OPTICS Colloidal Silica (3%) in ethanol	AMPLIFIER WINDOWS Colloidal Silica (2%) in sec-butanol	KD*P HMDS Treated Silica (10%) in decane	KDP Colloidal Silica (9%) in sec-Butanol (deammoniated)	KDP/KD*P GR650 (3.3%) in ethanol/sec-butanol
Final Composition						
SiO_2	wt%	3%	2%	10%	9%	3.3%
Ethanol	wt%	96.03%	13.89%	-----	90.97%	29.94%
H_2O	wt%	0.12%	0.08%	-----	0.03%	----
NH_3	wt%	0.85%	0.56%	trace	0%	----
sec-butanol	wt%	----	83.47%	-----	----	66.74%
Decane	wt%	----	----	90.00%	----	----
Particles						
Particle Size[1]	nm	21.0	14.3	27	14.8	----
Polydispersity Index[1]		0.6	1.1	1.2	0.6	----
Particle density[2]	cm^{-3}	2.5E+15	5.3E+15	3.8E+15	2.2E+16	----
Surface Properties[3]						
% OH	%	72%	nm	27%	34%	----
% OCH_2CH_3	%	28%	nm	39%	66%	----
% $Si-(CH_3)_3$	%	0%	nm	35%	0%	----
Solution						
Density	gm/cm^3	0.802	0.808	0.785	0.838	nm
Viscosity[4]	cP	1.32	nm	1.13	nm	nm
Solids loading (air dried)[5]	wt%	3.48	2.36	12.98	10.62	nm
H_2O content[6]	gm/cm3	0.95	nm	trace	0.22	
pH[7]		10.5	9.6	>8	6.9	nm
Transmission (300 nm)	%	79%	87%	73%	67%	nm
Preparation Time	days	3.0	4.0	21	5	1
NH_3 concentration[8]	moles/liter	0.39	0.33	----	0.06	----
Hydrolysis Kinetic Constants[9]						
First hydrolysis	liter/(mole-hr)	0.091	0.091	----	----	----
Second hydrolysis	liter/(mole-hr)	1.75	1.75	----	----	----
Air Dried Solid						
Si-O-Si Bonding[10]	----					
Q^1	%	0	nm	0	trace	0.0
Q^2	%	3.1	nm	3	2.7	0.0
Q^3	%	34	nm	15.3	43.3	0.0
Q^4	%	62	nm	73.9	54.0	0.0
M^1	%	0	nm	7.8	0.0	0.0
T^1	%	0	0.0	0	0.0	0.0
T^2	%	0	0.0	0	0.0	38.7
T^3	%	0	0.0	0	0.0	61.3
SURFACE AREA[11]	m^2/gm	606	nm	437	540	NA
FILM						
QA thickness[12]	Angstroms	2020	2270.0	2250	2260	2200
QA index[12]		1.167	1.210	1.230	1.210	1.420
1ω spin coat rate (Si conc)[12]	rpm	500 (1.5%)	600 (2 %)	2400 (10%)	1500 (3%)	600 (3.33%)

Footnotes for Table 2

(1) Measured using Dynamic Light Scattering (See Section 7.1)

(2) Calculated using average particle size and solids loading
(3) Measured using H MAS NMR (See Section 7.6
(4) Measured using rotating cylinder viscometer (Brookfield)
(5) Weight of air dried sol/ weight of original sol (See Section 7.7)
(6) Measured using Infrared Spectroscopy (See ref [1])
(7) Measured using standard pH electrode (See Section 7.4)
(8) Measured by titration (See Section 7.4)

(9) Measured using kinetic growth model (See ref [1])
(10) Measured using Si MAS NMR (Section 7.5)

(11) Measured by N_2 adsorption BET Method

(12) Measured by ellispsometry (Section 7.2)

2.0 SOLUTIONS FOR FUSED SILICA OPTICS

2.1 Colloidal Silica (3%) in Ethanol

2.1.1 Preparation Procedures (Laboratory Scale)

Batch size: 2 mole SiO_2 (120g in 2000g)
Concentration: 3% SiO_2

Batch:

Tetraethylsilicate (TEOS)	416 g
Ammonium hydroxide solution (30%)	118.8 g
Ethanol (EtOH)	3464 g

Equipment needed:

a) 5-liter single neck round bottom flask (fitted with a ground glass stopper)
b) cork stand for a 5 liter round bottom flask
c) 250 ml and 600 ml pyrex beakers
d) disposable pipettes (VWR 14672-608) and rubber bulbs (VWR 56311-049)
e) electronic balance (better than ± 0.1 gm)
f) glass storage bottles

Procedure:

1) Clean the 250 ml beakers and 5 liter flask using a dilute HF solution if needed (see procedures in section 8).
2) Filter all ethanol in a stainless steel filter housing with a 0.2 um filter (see section 9.0 for details).
3) Collect ethanol in a 2 liter glass bottles.
4) Measure the weight of the empty 5 liter flask on balance.
5) Add 3464 g of EtOH filtered to the flask.
6) Add 118.8 g NH_4OH into the beaker. It is recommended that this procedure be carried out in a fume hood. Measure weights on the balance when the fume hood is off.
7) Pour the NH_4OH solution into the flask and gently swirl the solution in the flask until it is homogeneous.
8) Add 416 g of TEOS to a 600 ml beaker; transfer to a 5-L flask.
9) Gently swirl the solution in the flask until it is homogenous. Do not mix with a magnetic stirrer.
10) Close the flask with a ground glass stopper.
11) Let the solution age for at least 3 days at room temperature.
12) Store in a closed glass container and label the solution with the name, date, and notebook number.
13) Perform the required QA measurements (listed in Section 6.0 and described in Section 7.0) and make sure they meet the requirements described in Section 6.0.
14) Paste a summary label stating QA results on the bottle.

2.1.1 Preparation Procedures (Production Scale)

Batch size: 7 mole SiO_2 / five gallon container (420g SiO_2 in 14kg)
Concentration: 3% SiO_2

Batch:

Tetraethylsilicate (TEOS)	1456 g
Ammonium hydroxide solution (30%)(NH_4OH)	415.8 g
Ethanol (EtOH)	12,124 g

Equipment:

a) 10 & 20 liter pressure vessel
b) 5 μm filters for pressure vessel
c) Detecto scale
d) Sartorius balance
e) 5 gallon glass carboy (VWR)
f) Plastic wrap (saran wrap)
g) 2000 ml Pyrex beaker

Procedure:

1) Preparations of this solution should be conducted in a Class 100 cleanroom or better (e.g. B391 cleanroom).
2) Open the top cap to the 10 & 20 liter pressure tanks and fill with EtOH from the 5 gallon container.
3) Close the top cap of both containers and pressurize each tank to 80 psi using the in-house N_2 supply.
4) Check to make sure the pressure tank has 5 μm filters connected to it.
5) Obtain 7-12 glass carboys (5 gallon size) depending on the amount of product required.
6) Clean <u>each</u> of the glass bottles by rinsing with EtOH from the 10 liter pressure tank. Use the spray nozzle on the pressure tank to spray EtOH on the inside surfaces of the bottle (use approximately 150 ml of EtOH). Mix the EtOH in the glass bottle by swirling the solution within the bottle.
7) Pour out the EtOH from the bottle into a waste container and let the glass bottle sit with an open top.
8) Place a glass bottle on Detecto scale and tare the scale. Using the 20 liter pressure tank, add 26.7 lb ±0.2 lbs of EtOH (12,124 g).
9) Remove the glass bottle from balance and cover it with plastic.
10) Weigh EtOH in to the remaining glass bottles following steps 8 and 9.
11) Pull out <u>unopened</u> bottle of NH_4OH.
12) Rinse out 2000ml Pyrex beaker with EtOH and let dry.
13) Put Pyrex jar on Sartorius balance and tare the beaker.
14) Weigh out 414 g of NH_4OH into the beaker.
15) Pour NH_4OH from the beaker into one of the 5 gal glass bottles.
16) Mix the solution by gentle swirling until homogeneous.
17) Repeats steps 14-16 for all the 5 gal glass bottles
18) Pressurize the TEOS tank with in house N_2.

19) Rinse a 2000 ml Pyrex beaker by rinsing it with EtOH from the 10 liter pressure tank. Note if the pressure in tank runs low, re-introduce pressure with in house N_2. Let the Pyrex beaker dry.
20) Tare the beaker on the Sartorius balance and add 1456 g of TEOS into the beaker.
21) Add the TEOS to the ammonia-ethanol solution in one of the glass carboys and swirl gently until homogenous.
22) Cover the glass bottle with plastic.
23) Repeat the procedure (steps 20-22) for the remaining glass bottles.
24) Cover the cap of glass bottle with plastic and tie wrap the plastic.
25) Label each bottle with the date and solution type.
26) Let the solution sit for at least 3 days.
27) Perform the required QA measurements (listed in Section 6.0 and described in Section 7.0) and make sure they meet the requirements described in Section 6.0.
28) Paste a summary label stating QA results on the bottle.

3.0 SOLUTION FOR AMPLIFIER WINDOWS

3.1 Colloidal Silica (2%) in sec-butanol

3.1.1 Preparation Procedures

Batch size: 0.67 mole SiO_2 (40 gm SiO_2 in 2000g solvent)
Concentration: 2% SiO_2

Batch:

Colloidal silica (3%) in ethanol	1333 g
Sec-butanol	~2600 g

Equipment:

a) 3 liter double-necked round bottom flask fitted with a ground glass stopper
b) cork stand for a 3 liter round bottom flask
c) Distillation setup (See Figure 1)
d) Electronic balance (better than ± 0. 1 g)
e) Teflon stirrer for 3 liter flask

Procedure:

1) Clean all glassware using a dilute HF solution if needed (see procedures in section 8).
2) Weigh out 1333 gm of Colloidal silica (3%) in Ethanol into a pre-weighed 3-L flask.
3) Insert a pre-weighed Teflon stirrer into flask.
4) Reflux the sol by placing the sol/flask in setup shown in Figure 1. Place Flask in distillation set-up by attaching ground glass joint of flask to the distillation head. Use a Teflon sleeve between the ground glass joints. Lower flask into silicone oil bath. Turn on the hot plate to 7-8 setting and then hook-up the ammonia collection in the manner shown in Fig. 1. Add water to the ammonia collection beaker. Make sure that the stir bar is rotating (setting 4); this will nucleate bubbles. The distillation will begin at ~68ºC, and bubbles should be seen coming into the ammonia collection beaker. The temperature will slowly rise to 78ºC as more ammonia is removed. Continue to distill and collect EtOH (900-1000 g) in the collection flask.
5) Add sec-butanol (~400 gm) to distillation flask. This can be performed by various methods. One suggested method is: Remove the 3 L flask from distillation set-up and add 400 gm of sec-butanol. Also, empty the collection flask into the designated waste bin. Reattach both flasks to the distillation set-up and distill.
6) Continue to distill and periodically add additional sec-butanol until a boiling point of 98^{o}C is reached. This boiling point ensures that essentially all the ethanol has been removed from the original sol.
7) Remove 3-L flask from the distillation setup and let cool while stirring.
8) Add sec-butanol to batch such that total batch weight is 2000 g.
9) Store in closed glass container and label the solution with the name, date, and notebook number.
10) Perform the required QA measurements (listed in Section 6.0 and described in Section 7.0) and make sure they meet the requirements described in Section 6.0.
11) Past summary label stating QA results on the bottle.

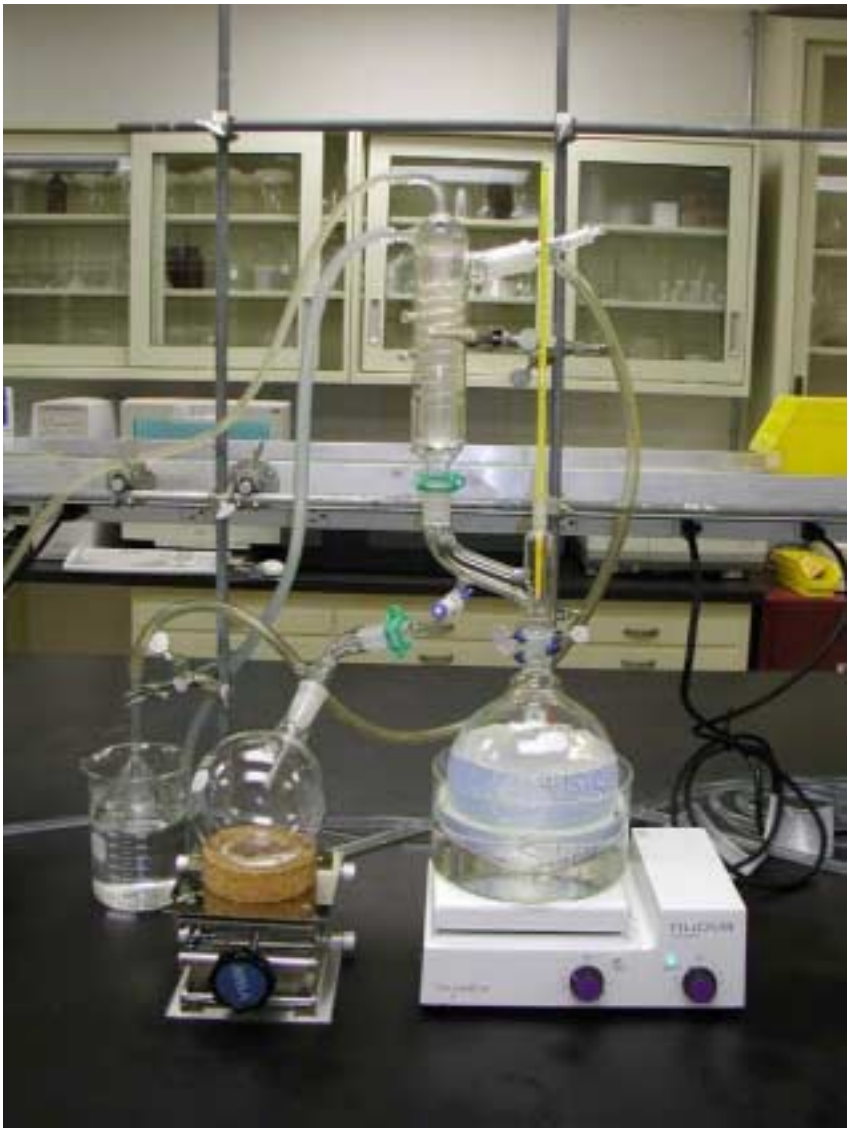

Figure 1: Photograph of distillation/reflux setup.

4.0 SOLUTIONS FOR KDP AND KD*P OPTICS

4.1 Colloidal Silica (9.0%) in sec-butanol (deammoniated)

4.1.1 Preparation Procedures

Batch size: 1.5 mole SiO_2 (90g SiO_2 in 1000g solvent)
Batch Concentration: 9 wt% SiO_2

Batch:

Colloidal silica (3%) in ethanol	3000 g
Sec-butanol	~1500 g

Equipment:

a) 3 liter double necked round bottom flask fitted with a ground glass stopper
b) cork stand for a 3 liter round bottom flask
c) Distillation setup (See Figure 1)
d) Electronic balance (± 0.1 g)
e) Teflon stirrer for 3 liter flask
f) N_2 gas supply filtered through carbon filter

Note: Typically several batches are made in parallel (but not required). Single QA can be performed on a mixture of batches.|

Procedure:

1) Clean all glassware using a dilute HF solution if needed (see procedures in section 8).
2) Weigh out 2000 g of Colloidal Silica (3%) in Ethanol into pre-weighed 3-L flask.
3) Insert a pre-weighed Teflon stirrer into flask.
4) Distill the sol by placing the sol/flask in setup shown in Figure 1. Place Flask in distillation set-up by attaching ground glass joint of flask to the distillation head. Use a Teflon sleeve between the ground glass joints. Also add a slight N_2 cover gas that is fed in on the second neck of the 3 liter round bottom flask. Turn on the hot plate to 7-8 setting and then hook-up the ammonia collection in the manner shown in Fig. 1. Add water to the ammonia collection beaker. Make sure that the stir bar is rotating; this will nucleate bubbles. The distillation will begin at 68ºC, and bubbles should be seen coming into the ammonia collection beaker. The temperature will slowly rise to 78ºC as more ammonia is removed. Continue to distill and collect EtOH in the collection flask.
5) After ~1000gm of EtOH is collected in the collection flask, remove 3 liter flask and add the remaining 1000 gm of Colloidal Silica (3%) in Ethanol. Also, empty out the collection flask to the designated waste container. (Make note of how much ethanol was removed)
6) Continue to distill EtOH until a total of ~2200 gm is removed from the original sol.
7) Remove 3 liter flask from distillation setup and add ~300 gm of sec-butanol. Continue to distill and repeat the additions of ~300 gm until a total of ~100 gm of sec-butanol have been added. Distill until a boiling point of 98^{o}C is reached. This procedure helps keep the batch size small and easier to remove any residual ammonia remaining in the batch.
8) After distilling, check the pH of the sol by taking 1.5 g of sol and putting it in 10 ml of water. If the pH is <7 stop; if not continue to reflux until pH <7.

9) Double check the weight of the solution. If the batch weighs less than 1000 gm, than add additional sec-butanol to achieve that weight. The resulting sol will be 9% silica.
10) Store in closed glass container and label the solution with the name, date, and notebook number.
11) Perform the required QA measurements (listed in Section 6.0 and described in Section 7.0) and make sure they meet the requirements described in Section 6.0.
12) Paste summary label stating QA results on the bottle.
13) Before this coating solution is used for coating an optic, it will be diluted to nominally 3.3% SiO_2 by the addition of sec-butanol.

4.2 HMDS treated silica (10%) in Decane

HMDS treated silica (10%) in Decane is the sol that will be used to coat some of the KDP optics (see Table 1). This sol is a chemically modified sol that has trimethylsilyl surfaces which make the sol very hydrophobic. This sol then provides a coating that prevents H_2O uptake which is known to cause etch pits. The preparation of HMDS treated silica sol (10%) in decane involves a two-step sol processs. Colloidal silica (3%) in ethanol is used as a starting sol for the preparation of the final HMDS treated sol.

4.2.1 Preparation Procedures

Batch size: 1.0 mole SiO_2 (60g SiO_2 in 600g solvent)
Batch Concentration: 10 wt% SiO_2

Batch:

Colloidal silica (6%) in Ethanol	1000 g
Hexamethyldisilazane (HMDS)	180 g
Decane	540 g
H_2O	30 g

Equipment:

a) 2 liter single necked round bottom flask fitted with a ground glass stopper
b) cork stand for a 2 liter round bottom flask
c) Teflon stirrer for a 2-liter flask (1 inch)
d) Electromagnetic stirrer plate
e) 250 ml beaker
f) 1000 ml beaker

Note: Typically several batches are made in parallel (but not required). Single QA can be performed on a mixture of batches.

Procedure:

1) Clean all glassware using a dilute HF solution if needed (see procedures in section 8).
2) Weigh out 1000 g of colloidal silica (6%) in ethanol into the pre-weighed 3 liter flask.
3) Insert a pre-weighed teflon stirrer into flask.
4) Distill off 500g of EtOH to concentrate the solution to 12% silica. To do this, assemble a distillation setup as shown in Figure 1. Place flask in distillation setup by attaching ground glass joint of flask to the distillation head. Use a teflon sleeve between the ground glass joints. Heat silicone oil at a setting of 7-8 on hotplate. Hook up ammonia collection in the manner shown in Fig 1: Add water in beaker. The distillation will start at about 68^{o}C, and bubbles should be seen coming out of the ammonia catch tube. You should see the bubbles getting small as they rise in the beaker, indicating that ammonia is dissolving into the water. The temperature will slowly rise to 78^{o}C as the ethanol distills out. Continue to distill until 500g of EtOH is collected in the collection flask. The entire distillation process should take about 4 hours. Periodically weigh the collection flask to check amount ethanol distilled.
5) Turn off heat to the silicone oil bath.

6) Removed the flask from the hot oil bath, carefully wipe off excess oil on bottom of flask, and let solution sit and cool to room temperature. Weigh solution and add ETOH if necessary to bring to 12 wt % silica in EtOH.
7) Verify that the weight of solution in collection flask matches expected amount to come off. Dispose of the distilled EtOH in a solvent waste container (it should have some ammonia in it).
8) Add 30 g of distilled water to the solution and stir with magnetic stirrer overnight (~16 hours).
9) Add 40 g of HMDS to the solution and stir with magnetic stirrer. After 30 minutes add another 50 g of HMDS. Let the solution stir ~24 hours.
10) Then add another 90 g of HMDS and stir for an additional 7-10 days.
11) Add 540 g of decane and distill as shown in Fig. 1 until all the ethanol, ammonia, and HMDS by-products are removed. Distillation starts at 48^{o}C and rises up to 100^{o}C. Continue until distillation stops and the temperature drops to <70^{o}C. This distillation takes approximately 6 hours.
14) Turn off the heat to the silicone oil bath.
15) Remove the flask from the oil bath, and let the solution sit and cool.
16) Verify that the weight of solution in the collection flask matches the expected amount to come off (~620 g). For guidance, Table 3 summarizes the batch composition at each step during the preparation of the HMDS modified sol.
17) If multiple batches were made; combine into one solution now
18) Store in a closed glass container and label the solution with the name, date, and notebook number.
19) Perform required QA measurements (listed in Section 6.0 and described in Section 7.0) and make sure they meet the requirements described in Section 6.0.
20) Paste a summary label stating QA results on the bottle (See Appendix).

Table 3: HMDS batch composition as a function of processing step

HMDS Batch Calculation During Processing							
Component	**As Batched**	**STEP 1**	**STEP 2**	**STEP 3**	**STEP 4**	**STEP 5**	**STEP 6**
	As batched composition for 6% sol	6% sol after aging (assume 100% complete)	12% sol	12% sol (H_2O added + HMDS added)	After HMDS reaction (Assume all water reacted, 9% of silica surface reacted, remainder reacts with EtOH)	Decane added	Distill out ethanol and NH_3
	(g)	(g)	(g)	(g)	(g)	(g)	(g)
ethanol	748	932	432	432	405	405	0
TEOS	208	0	0	0	0	0	0
NH_3	2.4	2.4	0	0	9.3	9.3	0
H_2O *	45	9	0	30	0	0	0
SiO_2	0	60	60	60	60	60	60
HMDS	0	0	0	180	0	0	0
$(CH_3)_3Si\text{-}OCH_2CH_3$	0	0	0	0	138	138	0
$(CH_3)_3Si\text{-}OH$	0	0	0	0	90	90	0
$(CH_3)_3Si\text{-}NH_2$	0	0	0	0	0	0	0
Decane	0	0	0	0	0	540	540
TOTAL	**~2000**	**~2000**	**503**	**713**	**711**	**1251**	**600**
[SiO_2] (wt%)	**0%**	**6%**	**12%**	**10%**	**10%**	**5%**	**10%**

* H_2O values are approximate

4.3 GR650 (3.3%) in ethanol/sec-butanol

Some of the KDP crystals are also coated with an undercoat called GR650 (Glass Resin 650). GR650 is a methyl silicone that is purchased from Techneglass as flakes and stored frozen. This material is then dissolved in alcohol solvents and coated onto KDP optics. Sometimes the coatings are cured (see Table 1). This section outline the preparation procedures for GR650 (3.3%) in ethanol/sec-butanol.

4.3.1 Preparation Procedures

Batch Size: 87.2 g GR650 in 2622 g
Concentration: 3.3%

Batch:

GR650	110 g
Ethanol	990 g
Sec-butanol	2208 g

Equipment needed:

a) 5-liter round bottom flask
b) Glass stopper that fits into the neck of the flask
c) Electronic balance (better than ± 0.1 g)
d) Teflon stir bar

Procedure:

1) Clean the 5 liter flask glassware using dilute HF solution if needed (see procedure in section 8).
2) Add 110 g of GR650 into flask.
3) Add filtered ethanol and Teflon stir bar into flask. Stir at room temperature until the GR650 dissolves (takes ~10 min).
4) Add 2208 gm of sec-butanol and stir.
5) Transfer solution to storage container.
6) Store in a closed glass container and label solution with name, date, and notebook number.
7) Perform required QA measurements (listed in Section 6.0 and described in Section 7.0) and make sure they meet the requirements described in Section 6.0.
8) Paste summary label stating QA results on bottle.

5.0 CHEMICAL AND EQUIPMENT DESCRIPTION

Table 4: Description of raw materials used in the preparation of all coating solutions.

Short Name	Chemical Name (CAS#)	Chemical Formula	Description	Vendor	Size	Product#
TEOS	Tetraethyl orthosilicate (76-10-4)	$Si(OC_2H_5)_4$	18,000 g UltrapureTM Double Distilled Grade Tetraethylsilicate (TEOS) filled in a 5 gallon SS MinibulkTM canister Contact Kelly Reynolds	ADCS P.O. Box Y 304 Industrial Blvd Burnet, TX 78611 (512) 756-7314 O (512) 418-8200 F (512) 418-8215	20 liters	UN1292 CZFI-TEOS
EtOH	Ethanol (64-17-5)	C_2H_5OH	Dehydrated Alcohol USP 200 Proof Punctilious	Quantum 11500 Northlake Dr. Cincinatti, OH 45249	5 gallons	
NH_4OH	Ammonium Hydroxide (1336-21-6)	NH_4OH	Ammonium Hydroxide 'Baker Analyzed' Reagent, 28.0-30.0%	Aldrich Chemical Company 1001 West St. St. Paul Ave. Milwaukee, WI 53233 (800)-558-9160 F-(800)-962-9591	1 L	338818
HF	Sulfuric Acid (8014-95-7)	HF	Sulfuric Acid 'Baker Analyzed' Reagent 95.0-98.0% (lot analysis on label)	VWR Scientific (J.T. Baker) PO Box 7900 San Francisco, CA 94120 1-800-932-5000	2.5 L	JT9681-5
HCl	Hydrochloric Acid (7647-01-0)	HCl	Hydrochloric Acid 'Baker Analyzed' Reagent 36.5-38.0% (lot analysis on label)	VWR Scientific (J.T. Baker) PO Box 7900 San Francisco, CA 94120 1-800-932-5000	2.5 L	JT9535-5
BuOH	Sec-butyl alcohol (78-92-2)	$CH_3CH_2CHOHCH_3$	Sec-butanol Certified (lot analysis on label)	Fisher Scientific 1-800-766-7000	4 L	01664-4
Decane	Decane (124-18-5)	$C_{10}H_{22}$	Decane 99 + % Anhydrous	Aldrich Chemical Company 1001 West St. St. Paul Ave. Milwaukee, WI 53233 (800)-558-9160 F-(800)-962-9591	2 L	457,116
HMDS	1,1,1,3,3,3-Hexamethyldisilazane	$(CH_3)_3SiNHSi(CH_3)_3$	Microprime HP primer HMDS Hexamethyldisilazane	MicroSi, Inc 10028 S. 51 St. Phoenix, AZ 85044 (602) 893-8898 F (602) 893-8693	1 Qt.	3, UN2924 11/8
Silicone Oil	Silicone Oil (63148-62-9)		Silicone Oil	Aldrich Chemical Company P.O. Box 355 Milwaukee, WI 53201 (800)-558-9160		14,615-3

Table 5: Description of equipment used in preparation of all coating solutions.

Item	Vendor	Contact Info	Description Size	Product #
pH meter	Cole Parmer	625 East Bunker Ct Veron Hills, IL (800) 323-4340	General Lab	E-05991-42
pH Buffer solution	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	pH 4 pH 7	34170-130 34170-127
10 liter pressure vessel	Millipore Corp	80 Ashby Rd. Bedford, MA 01730 781-533-6000	Stainless steel vessel that can be pressurized	xxx6700 P10
20 liter pressure vessel	Millipore Corp	80 Ashby Rd. Bedford, MA 01730 781-533-6000	Stainless steel vessel that can be pressurized	xxx6700 P20
Glass Pre-Filter	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	100 Pack 142 mm Gellman Sciences	A/E 61636 A/D 28150-996
5 um filters for pressure vessel	Millipore Corp	80 Ashby Rd. Bedford, MA 01730 781-533-6000	Mitex Membrane Filters, 25 mm, 5.0 um pore size	LSWP 01300
Disposable pipettes	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	Glass Pipets 5.75” Glass Pipets 9.00”	53499-630 53499-632
Glass storage bottles	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	2 L 1 L 250 ml	16157-227 16157-191 16157-136
5 gallon glass carboy	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	Bottle, carboy, 5 gallon	27003-520
Glassware (beakers, flasks, reflux station glassware, etc)	Ace Glass	P.O. Box 688 1430 Northwest Blvd Vineland, NJ 083-0688 (800) 223-4523	----	----
1L millipore filtration system	Millipore Corp	80 Ashby Rd. Bedford, MA 01730 781-533-6000	Filtration system, 142 mm	YT30142 HW
Volume burette	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	50 ml	17452-313
Weigh Bottles	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	30 ml	16713-127
Rubber bulbs	VWR	P.O. Box 7900 San Francisco, CA 94120 (800)932-5000	1 ml	56311-027
Nylon Filters	MSI	Westboro, MA C1518 1-800-444-3212	Magna-R Nylon 0.22μm 142mn	P02SP1422

6.0 QA SPECIFICATIONS OF ALL SOLUTIONS

Table 6 lists the specifications for all the coating solutions. Each solution must fall in the range of values reported for each property in order to "pass" as a good solution. Note that some of the procedures are required and some are optional for each of the coating solutions.

List of QA measurements:

1) Particle Size Analysis (see Section 7.1)
2) Refractive Index and Thickness (see Section 7.2)
3) Transmission Spectra (see Section 7.3)
4) pH / Titration (see Section 7.4)
5) ^{29}Si MAS NMR (see Section 7.5)
6) H MAS NMR (see Section 7.6)
7) Solid contents (see Section 7.7)

Table 6: Summary of required and optional QA procedures for all coating solutions

	QA #				
	Colloid Silica (3%) in ethanol	**Colloid Silica (2%) in sec-butanol**	**Colloid Silica (9%) in sec-butanol (deammoniated)**	**HMDS treated silica (10%) in Decane**	**GR650 (3.3%) in ethanol/ sec-butanol**
QA PROCEDURES REQUIRED	**1,2,3**	**1,2,3**	**1,2,3,4**	**1,2,3,5**	**2,3,7**
QA PROCEDURES (OPTIONAL)	**4,7**	**4,7**	**6,7**	**5,7**	**5,6,7**

Table 7 lists the specifications for each of the coating solutions for each of the QA measurements. The shaded cells signify that the QA measurement is required. The ranges for the specification are set generously with respect to previously measured samples. Typically, the ranges are set at the full range of deviation in the measurements for a series of measured samples. The specifications are set to control reproducibility, not necessarily to check if a solution is ‘good’ or ‘bad’. This is because we do not yet have information that a coating sol is ‘bad’ if it is out of specification on many of the QA measurements. Details of how each of the QA procedures should be performed are described in the next section (Section 7.0).

Table 7: Summary of QA specifications for all coating solutions

Property	QA PROCEDURE #	Specification				
		Colloidal silica (3%) in ethanol	**Colloidal silica (2%) in sec-butanol***	**Colloidal silica (9%) in ethanol /sec-butanol (deammoniated)***	**HMDS treated silica (10%) in Decane***	**GR650 (3.3%) in ethanol/ sec-butanol**
Unimodal Particle Size	1	**20± 3nm**	**14**	**6 nm**	**25 nm**	---
Test Film Index	2		**1.209**	**1.1833**	**1.218 ± .01**	**1.420 ± .01**
Test Film Thickness	2	**2750 ± 50 Å 2780 ± 100Å**	**2270Å**	**2794 Å**	**2150**	**2125 ± 50 Å**
300 nm Transmission	3	**≥79%**	**≥87%**	**≥73%**	**≥66%**	
pH	4	10.5	---	**6.9**		---
Ammonia Concentration	4	0.39 M	---	**0.06 M**	---	---
% trimethylsilyl modified	5	---	---	---	**8% of Si**	---
% Silanol surface	6	---	---	---	---	---
% Solids	7	3.48	2.36	10.8	13.50	---

7.0 QA PROCEDURES

The following section contains the QA Procedures for all the coating solutions. The QA procedures are established to maintain reliable/reproducible coating solution delivery. There are 7 different QA procedures that are either required or optional. A description of what QA is to be performed on which coating solution and the specifications for passing are given in the previous section (Section 6).

7.1 Particle Size Analysis

The following QA procedure is to measure the average particle size and particle size distribution of each of the colloidal sols. The measurement is carried out by dynamic light scattering using a commercial unit (Coulter N4 Plus). The technique measures the fluctuations in scattered light intensities in a colloidal solution. The light fluctuations can be than used to calculate the velocities of the colloidal particles and then the particle size of the colloid.

Equipment:

a) 1 cm plastic disposable cuvette (all sides polished)
b) few ml of sol to be analyzed
c) Coulter N4 Plus particle size analyzer
d) Diluting solvent for colloid sol

Procedure:

1) Turn on Coulter N4 Plus (Locate in B298 R174) by flipping the power switch on front of the unit. Let unit warm up for 15 minutes.
2) Prepare the sample by adding the proper amount of sol into a plastic cuvette. Note a dilution may be necessary. The amount of dilution for each specific sol is specified in Table 8 [4].
3) Turn on the computer connected to the N4 Plus and run the program “N4Plus.exe”
4) Press “123” shortcut button located near the top of the screen.
5) Enter sample information as directed in the pop up window, and then press the “Next” button
6) Select the diluent in the next pop-up window. The diluent chosen should be the same as the solvent that is present in the sol being analyzed (e.g. ethanol, decane, or sec-butanol).
7) Under “Profile-name”, select “QA-TS”. This brings up the standard measurement conditions that is used for all QA
8) Place the cuvette (containing the solution) into the sample chamber of the N4 Plus. Make sure that the sides of the cuvette are clean and dry to the eye.
9) Press “Next” on the next pop up menu.
10) The N4 Plus will then check the intensity of the signal. Make sure the intensity matches that reported in Table 8 [4].
11) If the counts are not in the desired range, a more concentrated (if counts are too low) or a more diluted (if counts are too high) solution will need to be made until the counts are in the desired range.
12) Press “start” if the signal gives the correct intensity.
13) The measurement will take approximately 10-15 minutes. After the measurement, record the value of average unimodal particle size and the average polydispersity index of the three

sample runs. If there is a large variation in the 3 sample runs; repeat the measurement to see if the variation is reduced.

14) Remove the sample cuvette from the sample chamber and dispose of the solution in the waste container. Thoroughly rinse the cuvette numerous times with additional dilutent and then dry the cuvette in air.
15) Turn off power to the N4 Plus and exit the N4 Plus program.

Table 8. Guidelines for amount of dilution and scattered intensity for performing particle size QA.

Colloidal silica sol	**Recommended range for scattered light intensity (counts/sec)**		**Typical dilution ****	**Time to reach equilibrium**
	Ideal	Range		
Colloidal silica (3%) in ethanol	**500,000**	250,000-750,000	x6	30 - 60 min
Colloidal silica (2%) in sec-butanol*	**500,000**	250,000-500,000	none	0 min
Colloidal silica (9%) in sec-butanol (demammoniated)	**500,000**	300,000-800,000	x3	0 min
HMDS treated silica (10%) in decane	**600,000**	500,000-1,000,000	x5	0 min

* 2% colloidal silica sol in 2-BuOH is measured without dilution and gives a light scattering intensity of 5×10^5.
** Diluted in the same solvent by weight.

7.2 Refractive Index and Thickness

The following QA procedure is to measure the refractive index at 632.8nm and thickness of a test film coated with the desired coating solution. The test film will be coated by spin coating, and the index and thickness will be measured by ellipsometry. The purpose of this QA is to check the reproducibility of the coating solution. This QA will indirectly probe the viscosity, solids loading, particle size, and particle-particle interaction of the coating solution.

7.2.1 Test film Preparation Procedure

Equipment:

a) SpinCoater (in B490 R1423B)
b) 1ml of coating solution
c) EtOH
d) Disposable glass pipette and rubber bulb
e) 2" silicon wafer
f) latex gloves

Procedure:

The power is normally left on for the spin coater. To check, look to see if rpm is displayed on the readout screen. The power switch (as well as all other controls) is on the left side toward the back.

1. Lift the spin table (plastic disc about 8” in diameter) and check that the o-ring is centered on the rotating platform. Remove the tape from the center of the spin table if it is there. This allows vacuum to hold the wafer in place during spinning. Then replace the table directly over the o-ring.

2. To check (or change) the program, the controller gives several options (1 = Prog #; 2= Run; 3 = Edit; 4= Set up). Press ‘#3’ followed by ‘enter’. Next press ‘#1’ and ‘enter’. Then successively press the ‘enter’ button to step through the program. When the cursor indicates a value that you want to change (e.g. rpm), use the numeric keys to change that number. Continue pressing enter until you have gone through the entire program and returned to the original screen.

3. After placing the sample in the middle of the spin table, turn on the vacuum by pushing ‘select’ ‘3’. Push gently downward on the spin table so it sits on the o-ring below it. You should hear a difference in the vacuum pump.

4. After turning on the vacuum pump check that the part is held in place by trying to move it sideways. Place the plastic cover over the spin table.

5. To run, push ‘# 2’ on the controller. Then push ‘select’ ‘1’ (spin table should move slightly) followed by ‘select’ ‘2’.

6. Check relative humidity and use N_2 saturated H_2O vapor to increase if rh is <40%.

7. Run one time without sol to check the rpm and that the optic sits correctly.

8. To dispense sol, fill the pipette full. Through a hole in the center of the plastic lid, dispense ~ 1.5 ml of sol onto the center of the optic with the spin coater revolving at full speed. Be sure to hold the pipette perpendicular to the surface of the optic. It is important not to let drops fall on the rotating surface. Note it is better to pipette on too much sol because the excess will spin off. You cannot go back and add more or you will get a non-uniform coating.

9. Let the sample continue to spin at full rpm for at least 5 min.

10. Press ‘reset’ to stop the optic from spinning. Then push ‘select’ ‘3’ to turn off the vacuum after rotation has completely stopped.

11. Remove coated sample.

7.2.2 Ellispsometry Measurement Procedures

Equipment:

a) ellipsometer (Jobin Yvon-Sofie, UVISEL)
b) coating to be analyzed (spin coated on a s Si water)

Procedure:

1. The ellipsometer (Jobin Yvon-Sofie, UVISEL) is located in B392 Cleanroom. The machine should be left running because it takes ~12 h for the electronics to stabilize. The lamp however is turned on/off each day. It requires 10 minutes to warm up. Leave the machine at 0% relative humidity overnight.

2. Introduce the sample into the in situ holder. To do this, carefully remove the 4 screws of the holder (it is heavy). Remove the sample holder from the machine, and stand it on its base. Place the sample in the holder with the surface to be examined facing downward. It is very important that the sample sit flat in the holder. For a Si wafer, place an optic on top to hold the wafer in place. Gently secure with the copper plate and four small screws. Return the holder to the machine and secure with the four larger screws. Only one alignment is correct so be sure to line up the two tape arrows.

3. Turn on the humidity probe attached to the in situ chamber after the sample chamber. Adjust the humidity by mixing the flow of dry nitrogen and nitrogen saturated with water vapor. It takes a few minutes to come to the desired humidity. Before and after each acquisition record the temperature and relative humidity displayed by the thermo-hygrometer. Make triplicate acquisitions at each desired relative humidity. Wait approximately five minutes between each acquisition.

4. The method for acquiring acquisitions is described in the ellipsometer's instrument's manual. In general the following steps should be followed.

    a) Scan the sample in triplicate at 0% and 90% relative humidity (as needed) to produce a series of data files.
    b) Using model SIO2SI (silica on Si) fit the 0% RH files (from 270-1700nm) to find the thickness of layers 1 and 2 and the volume of layer 2.
    c) Holding the thickness of layers 1 and 2 constant fit water only to find n for all files.
    d) Assume the water fraction = 0 at 0% RH; subtract the 0% index from the composite index from Elli to get the fraction of water in the film at 95%RH.
    e) Using a water index of 1.33, void index of 1.0, and a void fraction of 1 – volume of layer 2, calculate the fraction of void filled by water.

    $$\text{Fraction of void filled by water} = \frac{\text{fraction of water in film}}{(0.33)(1 - \%SiO2)}$$

7.3 Transmission Spectra

The following QA measures the optical transmission of a sol solution as a function of wavelength. The purpose for performing this QA is two fold: 1) To double check the particle size analysis by observing any scattering in the UV (higher scatter would reduce the % transmission) [2]; and 2) to check to see if there are any absorbing contaminants (organics or metal contaminations) in the solution. For simplicity we will just note that 300nm is a good wavelength to use for QA since it is sensitive to optical scatter and some of the common absorbing species found in the sol in the past.

Equipment:

a) Shimazdu UV- VIS Spectrometer (B490 RM1423B)
b) Matching Pair of Quartz cuvettes
c) Disposable glass pipette and rubber bulb

Procedure:

1) Clean quartz cuvettes by rinsing them with EtOH or use HF cleaning procedure if necessary (see sec.8).
2) Turn on Shimazdu UV-Vis Spectrometer (15 min warm up time).
3) Run UVPC software on computer.
4) After self calibration, set speed to "very slow" in configure menu.
5) Run baseline without anything in the sample chamber.
6) Fill one quartz cuvette with solvent in which the sol is contained and fill the other with the sol to be analyzed. Place the solvent/quartz cuvette in the reference beam and the sol/quartz cuvette in the sample beam inside the Shimazdu sample compartment.
7) Make sure that transmission at 1100 nm is between 99.9 and 100.1%. If not, clean the surface of the cuvettes and the transmission should fall in that range.
8) After the scan, save the file and write down the transmission at 300nm in the notebook.
9) Clean quartz cuvettes and turn off the spectrometer.

7.4 pH / Titration

The purpose for the following QA is to measure the ammonia concentration in a coating solution. This QA is especially important for colloidal silica (3%) in ethanol/sec-butanol (deammoniated) where the amount of final ammonia content needs to be minimized. For this sol, the initial pH of the sol before titration must be ≤ 7.

Equipment/Chemicals:

a) 30-50g of sol to be analyzed
b) DI water
c) Ring stand
d) Magnetic stirrer
e) Volume burette
f) pH buffer solution
g) pH meter/electrode
h) Magnetic stirrer
i) 2-250ml beakers
j) pH indicator (Bromophenol Blue) (optional)
k) 0.1 N and 1.0 N HCl solution (see section 5.0)

Procedure:

1) Clean the pipet and beakers using standard cleaning procedures.
2) Fill one beaker with DI water (use for rinsing pH electrode).
3) Add ~30ml of DI water to the other beaker.
4) Add ~5-6ml of the sol to be analyzed (some sols will precipitate when mixed with water) (record exact amount of sol added).
5) Mix water/sol mixture using a magnetic stirrer.
6) Calibrate the pH meter at pH 4.00 pH 7.00 using buffer solution.
7) Rinse pH electrode.
8) Measure initial pH of water/sol mixture (keep mixing during measurement). Record pH. Use the titration worksheet.
9) Add 0.1 N HCl (use 1 N HCl if expecting large concentrations of ammonia in sol) into the volume burette.
10) Record the initial volume of 0.1 N HCl in volume burette.
11) Slowly add (dropwise) 0.1 N HCl to the beaker containing sol/water mixture. Monitor the pH until it reaches a pH of 2.0.
12) Record the final volume of 0.1 N HCl in volume burette.
13) A suggested worksheet is provide to calculate the ammonia concentration (see 7.4.1)

7.4.1 Titration worksheet

Date _____
Sol # _____
Description _____
Measurement by _____

Wt % Silica in sol = _____ % (wt %)

Sol density = _____ g/cm^3 (P_{sol})

ml of sol added to beaker _____ ml (V_{sol})

ml of water added to beaker _____ ml

Concentration of acid _____ mole/liter (C_{acid})

Initial reading on titrating pipet _____ ml (V_i)

Final reading on titrating pipet _____ ml (V_f)

Initial pH of sol _____

Final pH of sol _____ (target 2.0)

Ammonia Concentration (C)

Ammonia concentration in solution $C = \frac{C_{acid}\ (V_i - V_f)}{V_{sol}}$ $C =$ _____ *mole / liter*

7.5 ^{29}Si MAS NMR

^{29}Si MAS NMR stands for Silicon Magic-Angle-Spinning Nuclear Magnetic Resonance. This technique is utilized to measure the types of silicate species present in the sol, and it is specifically useful for measuring how much trimethylsilyl functionalization has taken place in HMDS treated silica (10%) in decane.

7.5.1 Sample Preparation Procedure

Using the same procedure outlined in section 7.7, dry the solution of interest to obtain a powder.

7.5.2 NMR Measurements

The ^{29}Si MAS NMR measurements should be conducted at Spectral Data Services, Inc (818 Pioneer, Champaign, IL, 61820, 217-352-7084, contact: Gary L. Turner).The measurements should be conducted on a 270 MHz spectrometer at a MAS spin rate of 4 kHz.

7.5.3 Data Analysis

Spectral Data Services will report a spectrum similar to the one shown in Fig. 2. The amount of trimethylsilyl functionalization can be calculated as the area under the 12 ppm peak (corresponding to amount of Si $(CH_3)_3$ species) divided by the total area of all the peaks).

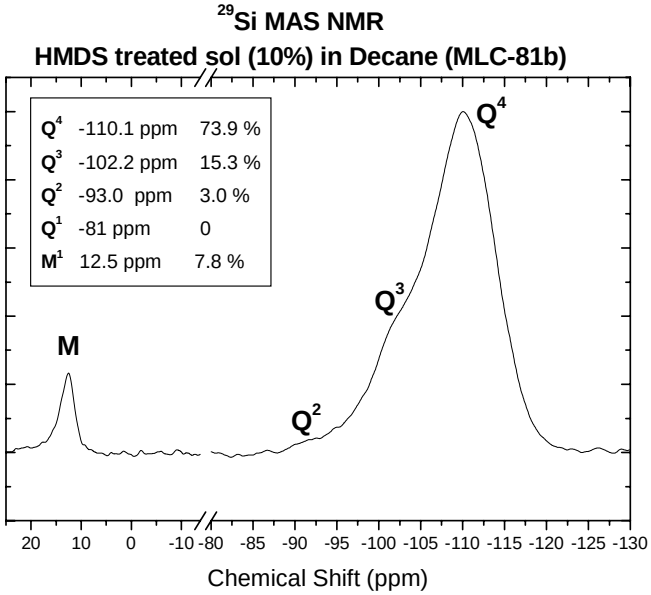

Figure 2. ^{29}Si NMR Spectra of dried HDMS treated silica (10%) in decane[3].

7.6 ^{1}H MAS NMR

^{1}H MAS NMR stands for Hydrogen Magic Angle Spinning Nuclear Magnetic Resonance. This QA provides quantitative information about the surface chemistry of the silica sols. This technique is specifically useful in characterizing the surface chemistry of the intermediate sol (colloidal silica (6%) in ethanol) to ensure that it has a high silanol surface. A high silanol surface on the colloid is required to ensure efficient trimethylsilyl functionalization during HMDS treatment [3].

7.6.1 Sample Preparation Procedures

Using the same procedure outlined in section 7.7, dry the solution of interest to obtain powder.

7.6.2 NMR Measurements

The H MAS NMR experiments should be conducted at Spectral Data Services, Inc. (818 Pioneer, Champaign, IL. 61820, 217-352-7084, contact: Gary L. Turner). The measurements should be conducted on a 370 MHz spectrometer at a MAS spin rate of 4.5 kHz.

7.6.3 Data Analysis

Spectral Data Services will report a spectrum similar to that shown in Fig. 3. Each peak in the spectra corresponds to a specific H containing surface species. The chemical shifts for the chemical species are shown in Table 9.

Table 9: H NMR chemical shift for different surface species.

Species	**Chemical Shift**
$-Si(CH_3)_3$	-0.2 ppm
SiOH	4.9 ppm
$Si-OCH_2CH_3$	0.97 & 3.56 ppm

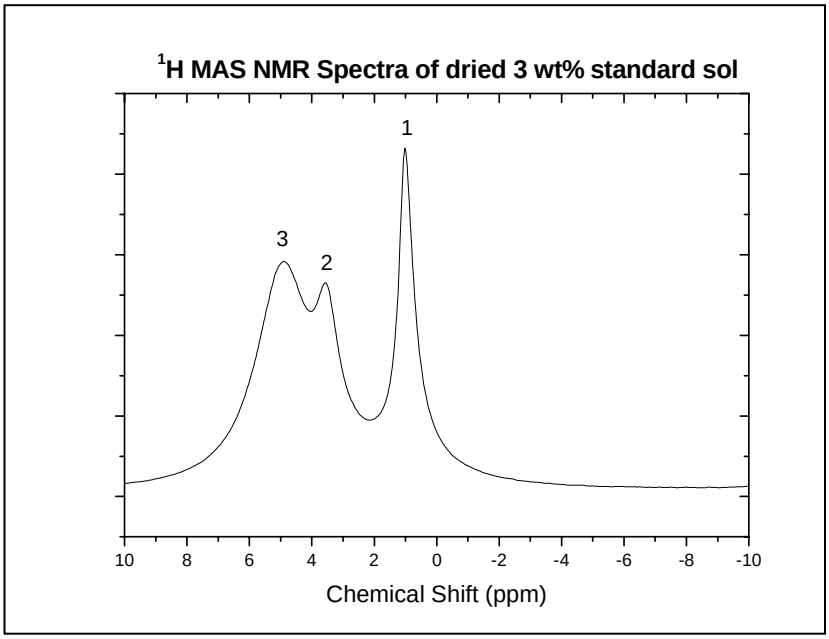

Figure 3: H MAS Spectra of a dried sample of colloidal silica (3%) in Ethanol. Peaks 1 & 2 are from protons in ethoxide surface species, peak 3 is from silanol surface species[3].

The area of each peak can be calculated by using a Lorentzian multi-peak curve fitting routine (use ORIGIN Software). Then the following equations can be used to calculate the % of each chemical species present:

$$\%\,Si(CH_3)_3 = \frac{A_{(-0.2\,ppm)/9}}{A_T} \bullet 100$$

$$\%\,SiOH = \frac{A_{4.9}}{A_T} \bullet 100$$

$$\%\,Si - OCH_2CH_3 = \frac{A_{0.97\,ppm/3}}{A_T} \bullet 100$$

where % $Si(CH_3)_3$, % SiOH, and % $SiOCH_2CH_3$ are the % of each of the chemical species present. $A_{-0.2ppm}$, $A_{4.9ppm}$ and $A_{0.97ppm}$ are the areas of the peak at the corresponding chemical shift. A_T is the total area of the spectrum. Further details about using H MAS NMR to evaluate surface chemistry of the sols can be found elsewhere [3].

7.7 Solids Contents

The following QA provides a quantitative measure of the solid loading in a particular coating solution.

Equipment/Chemicals:

a) 10-30 g of solution to be analyzed
b) weigh glass bottles with cap
c) fume hood
d) balance (± .0001g)
e) drying oven

Procedure:

1) Measure the weight of the weighing bottles with the caps on (M_{bottle}).

2) Add the sol to be tested to the weighing bottle and immediately replace the lid.

3) Re-weigh the bottle plus sol. ($M_{bottle\ \&\ solution}$)

4) Place the weigh bottle (lid removed) in the fume hood. Allow the solvent to evaporate (24-120 h).

5) Heat bottle and dry sol at 120ºC overnight for at least 5 hr.

6) Replace the lid and re-weigh the bottle plus dry sol after cooling. ($M_{bottle\ \&\ dry\ sol}$)

7) Calculate the solids content as:

$$\frac{M_{bottle\&drysol} - M_{bottle}}{M_{bottle\&solution} - M_{bottle}} \bullet 100\%$$

8.0 GLASSWARE CLEANING PROCEDURES

All pyrex glassware (except for the borosilicate VWR 5 gallon containers) used in the synthesis and storage of the sol coating solutions should first be cleaned using 5% HF solution. The procedure for doing this is given below.

1) This procedure should be carried out in a hood and proper laboratory attire should be worn (e.g., gloves, safely glasses). Make sure calcium glucanate is available in the case of a spill.
2) Prepare a 5% HF solution. This solution should be made periodically and need not be prepared every time glass cleaning is required. In a 1 liter plastic jug, add ~50 ml of concentrated HF (J.T. Baker). Then fill the jug to approximately 1 liter with DI water and cover with a plastic lid.
3) To clean glassware, fill (beakers, flasks) with or dip (stoppers, ground glass joints, condenser tubes) the glassware into the HF solution. Gently, swirl the solution around (typically for 10-20 seconds for most glassware). Swirl the solution until inside surface of flask is clear of 'gel marks' and solution evenly wets the inside surface.
4) Pour the 5% HF solution back into the 1 liter plastic jug or remove the glassware from the 1 liter flask. Cover the 1 liter plastic jug. Note it is not recommended to dip the beakers and flasks into the HF solution because the solution will remove any markings on the outside surface of the glassware such as volume scale markings.
5) The glassware should show a uniform wetting of the surface, indicating that all the surface have been cleaned. If this is not the case, repeat steps 3 and 4.
6) Rinse with plenty of DI water.
7) Then rinse with ethanol several times. This allows fast drying of the glassware. Store the glassware to dry for 10-15 minutes. One can blow dry nitrogen to speed up the drying process.

9.0 SOLUTION FILTERING PROCEDURES

Equipment:

a) 1 L millipore filtration system
b) 142 mm Nylon 0.22 μm filter (MSI)
c) 142 mm Type A/E or A/D Glass Pre-filter (Gelman Sciences)
d) ≈1000 ml flask (temporary collection flask)
e) Sol collection bottle (1L)

Procedure:

1) Assemble millipore filtration system by inserting 0.22μm filter and glass pre-filter between the stainless steel concentric support ring and the gray mesh plate. Tighten the bolts to enclose unit.
2) Rinse the filtration system by passing the solvent in which the sol is contained through it. Pour ethanol into the top of the filtration system, and place a collection flask below the millipore unit.
3) Turn off N_2 pressure after ethanol stops coming out from the bottom of the millipore system. Then turn off N_2 supply and release the pressure in the millipore system using the release value.
4) Open the top cap of the milipore system and then pour the sol to be filtered into the milipore system. Insert a collection bottle below the system. Close the top cap and add N_2 pressure as before.
5) Continue to filter until no more solution is removed from the filtration system. Then close and label the collection bottle.
6) Turn off N_2 pressure in the same manner as before. Rinse the inside chamber with ethanol and throw away glass pre-filter and filter.

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